

# Novel Sorbents Based on Silica Coated with Polyethylenimine and Crosslinked with Poly(carboxylic acid): Preparation and Characterization

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**ABSTRACT:** Novel sorbents based on silica coated with polyethylenimine (SilPEI) and crosslinked with poly(carboxylic acid) were prepared and characterized. These sorbents are to be used for heavy metal decontamination of aqueous solutions and have to be prepared in easy and ecological ways. A part of the carboxylic moieties [from ethylenediaminetetraacetic acid (EDTA) or citric acid] reacts with some of the amine groups of polyethylenimine, initially coated onto the silica, whereas the other part remains free for further metal complexation. By changing various parameters (temperature, pH, presence or absence of an amide-forming agent), the conditions to prepare the best sorbent—

that is, the sorbent exhibiting both a high capacity for metal complexation and good stability in an acidic medium (conditions for metal desorption or stripping)—were defined. The sorbent was prepared by a reaction of 1 g of SilPEI and 1 g of EDTA in water at 0°C, pH 6, during 10 h, using 0.5 g of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride as a coupling agent. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 799–805, 2003

**Key words:** polyamines; silicas; coatings; adsorption; metal-polymer complexes

## INTRODUCTION

The use of silica as a matrix for the immobilization of functional polymers has been developed for various applications such as chromatography, catalyst supports, and water purification.<sup>1,2</sup> The polymer can be covalently grafted or coated onto silica. The immobilization of amino and carboxylic groups by reacting them covalently with silica gels has already been studied.<sup>3–4</sup> In recent years the preparation and characterization of sorbents based on the coating of polyamines on silica have been described.<sup>5,6</sup> More recently, the approach taken was to first coat silica with polyethylenimine (PEI) and then to anchor PEI onto silica by a mild crosslinking reaction. Such sorbents were prepared for use in metal chelation for the purpose of decontaminating effluents containing heavy metals.<sup>7</sup> PEI is very interesting for its high metal chelation ability and its water solubility. Unfortunately, during the usual crosslinking reactions, which use amine-reactive bifunctional agents such as epichlorohydrin, diepoxides, or dialdehydes,<sup>8–10</sup> some of the amine groups of PEI become unavailable for further metal

complexation. To overcome the lack of chelating groups, multifunctional crosslinking agents like ethylenediaminetetraacetic acid and citric acid may be used. A part of their tetra- or tricarboxylic functionality could react with the amino groups of PEI while some carboxylic moieties would remain available for further metal chelation.

The aim of the present work was to synthesize a range of chelating materials obtained by varying the conditions of reaction and taking into account economic and environmental considerations. These sorbents should exhibit high metal uptake ability and chemical stability, especially in an acidic medium, which is necessary for metal recovery and cycling uses.

## EXPERIMENTAL

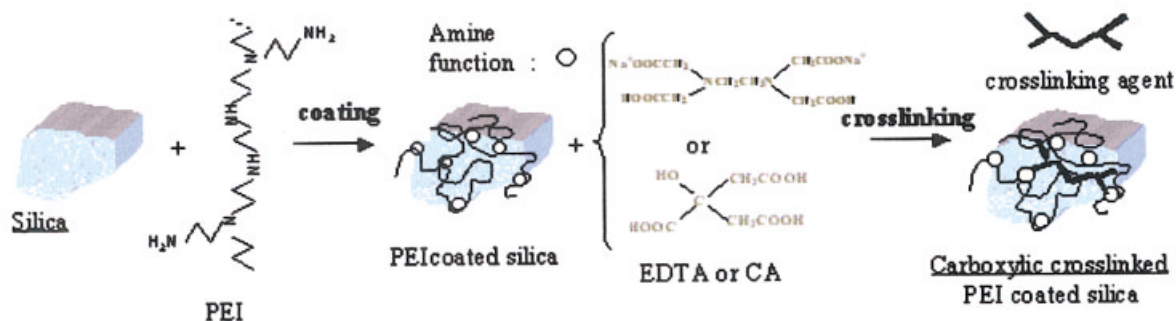
### Materials

Porous silica gel (Sil) is a commercial product from Aldrich (35–75  $\mu\text{m}$ , specific area of 270  $\text{m}^2/\text{g}$ , and mean pore diameter of 150  $\text{\AA}$ ).

Polyethylenimine (PEI) is a commercial branched polymer (Aldrich) with 50%, 25% and 25% of secondary, primary, and tertiary amino groups, respectively.

Disodium salt of ethylenediaminetetraacetic acid (EDTA) dihydrate, citric acid (CA) monohydrate, and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hy-

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Scheme 1 Two-step synthesis of the sorbents.

drochloride (EDAC) were purchased from Aldrich. They were used without any further purification. Adjustments of pH were made with 0.1N NaOH and 0.1N HNO<sub>3</sub>.

### Preparation of sorbents

It consisted of two steps: (1) the coating of silica by PEI, which has already been described,<sup>11</sup> and (2) the immobilization through the carboxylic agent (EDTA or CA), which was performed as follows:  $x$  grams of EDTA (sodium salt form) or CA were dissolved in 50 mL of water; then 1 g of SilPEI was added and the pH adjusted to 6. The mixture was stirred for a given time (from 0 to 96 h) under a controlled temperature (0°C or ambient temperature). The modified sorbent was then filtered from the solution and washed successively with 100 mL of water and 100 mL of acetone. It was finally dried under vacuum overnight at 60°C. When a coupling agent was used, it was added and allowed to react for 30 min under stirring before the addition of SilPEI.

### Characterization

The IR spectra of the sorbent in KBr pellets were obtained with a Perkin–Elmer spectrometer (Spectrum One) in transmission mode.

Solid-state <sup>13</sup>C-CPMAS spectra were recorded with a Bruker Biospin Avance 300 spectrometer operating at 75.47 MHz with a high-power crosspolarization sequence, using two proton power levels for CP and decoupling. The following conditions were applied: relaxation delay of 5 s, <sup>1</sup>H 90° pulse length of 3.8 μs, contact pulse of 1 ms, and spin rate of 4000 Hz. The sorbents were placed in a ZrO<sub>2</sub> rotor (4 mm in diameter). The measurements were performed at 303 K.

Elemental analysis was performed by the micro-analysis service of CNRS (Vernaison, France).

Organic materials immobilized onto silica were quantified by thermogravimetric analysis (TGA) under air at a heating rate of 10°C/min (TGA 51, Shimadzu).

Specific areas and pore size distributions were determined by nitrogen adsorption (Sorptomatic 1990, Thermoquest).

## RESULTS AND DISCUSSION

The purpose of this investigation was to find the best conditions for immobilizing complexing and chelating groups via an easy way of synthesis.

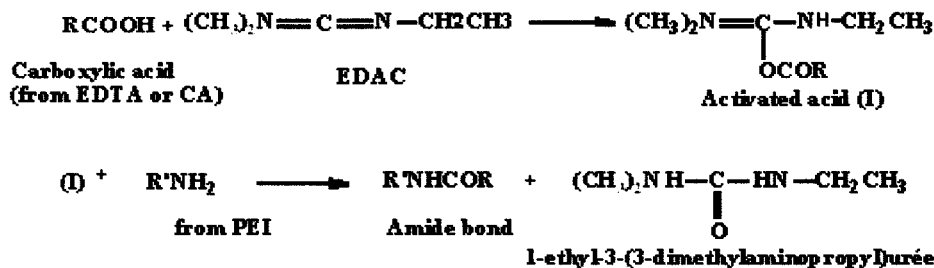
The coating method is more restrictive in the type of functional groups that can be adsorbed. For example, it is impossible to coat acidic compounds onto silica. In this study, an alternative method was adopted, which added an intermediate step, consisting of the coating of silica by PEI, and a second reaction step with acid carboxylic moieties, as represented in Scheme 1.

Because amide bond formation does not occur spontaneously except at high temperature, the acid group has to be converted to an activated form. The condensation of the amino groups of PEI and the carboxylic groups of EDTA can be activated by a carbodiimide reagent (Scheme 2). In peptide synthesis dicyclocarbodiimide remains the most popular *in situ* activating reagent. It is appropriate for use in an apolar environment. Over the years 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDAC) has emerged as the reagent of choice for amide coupling reactions in an aqueous phase (with good solubility and easier separation of the urea and *N*-acylurea as by-products of the condensation).<sup>12,13</sup>

The use of this agent for coupling amine and carboxylic groups belonging to molecules coated onto a solid surface (in a particular silica) is an original way, which needed optimization. Our aim was also to compare sorbents obtained without EDAC (SilPEI/EDTA, for example) and with EDAC (SilPEI/EDTA/EDAC).

### Influence of reaction parameters

The effects of reaction time, pH, temperature, and amount of reagents were studied.



Scheme 2 Activation of acid-amine condensation by EDAC.

Reconditioning is an important criterion for the reuse of the sorbent. In metal complexation regeneration is generally carried out by acid washing. So for each synthesis the amount and composition of the coated organic phase was compared before and after acid washing (0.5N HNO<sub>3</sub>, *t* = 20 min) to test the chemical stability of a given sorbent.

#### Effect of reaction time

Figure 1 shows that a contact time of 24 h is necessary to attain the maximum amount of organic phase coated onto silica. This value was calculated from TGA analysis. Which parts were EDTA coated and which PEI coated could be evaluated by the difference. The use of EDAC permitted not only an increase in the rate of coating (Fig. 1) but also prevented desorption during acid treatment (Fig. 1). As expected, EDAC favored the formation of a covalent amide bond that stabilized the organic phase around the silica. Without a coupling agent, EDTA probably interacted with PEI by ionic bonding only (NH<sub>3</sub><sup>+</sup> and COO<sup>-</sup>).

#### Effect of reagent ratios

Table I shows a comparison of the results obtained with the different reagent ratios. The highest amounts of organic phase remaining adsorbed after acid treat-

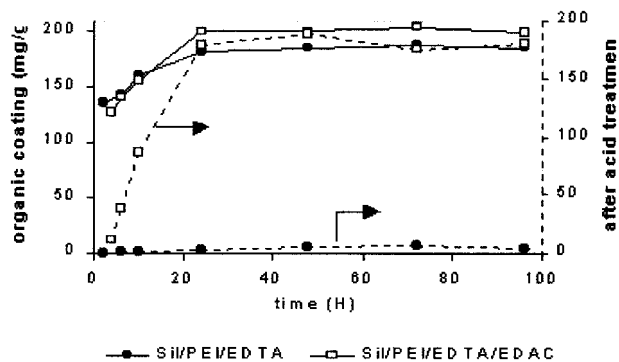


Figure 1 Effect of reaction time on organic coating for SilPEI/EDTA and SilPEI/EDTA/EDAC (1 g of SilPEI, 1 g of EDTA, 1 g of EDAC; *T* = 25°C, air; → remaining phase after acidic treatment).

ment were obtained for three reagent ratios. Increasing the amounts of EDTA and EDAC beyond 1 g of EDTA (2.68 mmol) and 1 g of EDAC (5.2 mmol) per 1 g of SilPEI (2.6 mmol of amine units) did not increase the weight of the coated phase. A plateau was reached, and this was consistent with the adsorption isotherms onto solid surfaces.<sup>14</sup> But the best system from an economical standpoint had a ratio of equal quantities of the three reagents (1 g:1 g:1 g). It led to a sorbent with a total organic phase of 190 mg, of which a minimum of 80 mg, or 0.21 mmol/g, was EDTA. Thus, only 8% of the initial EDTA molecules took part in the condensation. It is more than likely that all four carboxylic groups did not react with the amine. So it can be expected that some amino and probably some carboxylic groups would still be free and available for further metal complexation.

#### Effect of pH

Figure 2 shows that the coating and crosslinking reactions were favored at intermediate pH values (5–7). In fact, there were two ionizable species: amines from PEI and carboxylic groups from EDTA. However, with an acidic or basic pH, one of the two species

TABLE I  
Effect of Reagents on Amount of Organic Phase Immobilized Before and After Acid Treatment (pH = 6, *t* = 24 h, *T* = 25°C, air) in the SilPEI/EDTA system

SilPEI (g)	EDTA (g)	EDAC (g)	Coated organic phase (mg/g)	
			Initial	After acid treatment
110 mg/g of PEI				
1	0.5	1	183	79
1	1	1	197	183
1	2	1	200	182
1	3	1	178	161
1	4	1	171	121
1	1	0.5	172	78
1	1	2	198	184
1	1	3	175	154
1	1	4	173	153
2	1	1	190	128
3	1	1	186	15
4	1	1	181	5

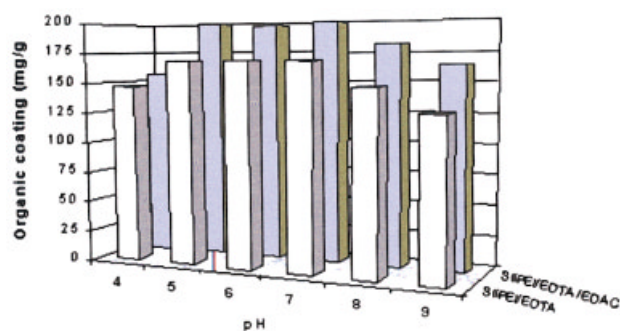


Figure 2 Effect of pH on organic phase fixation.

carried a majority of the same charge, creating electrostatic repulsions, less favorable for coating and crosslinking.

#### Effect of temperature

*Test at high temperature:* To avoid using EDAC for the acid-amine coupling, another way of fixing the organic phase onto silica can be employed: to react the carboxylic groups of the acid and the amine with each other to form an anhydride. This reaction needs a high temperature. To promote acid-acid condensation, after coating in water at ambient temperature, the sorbents were brought to a high temperature (120°C and 160°C) in an oven for various reaction times (15 min, 60 min, or 24 h) and in the presence of, or without, a catalyst,  $\text{Na}_2\text{HPO}_4$  (3% weight).  $\text{Na}_2\text{HPO}_4$  is known to be a catalyst for anhydride and ester formations, but the mechanism for this is not yet known.<sup>15</sup> The results are shown in Figure 3.

Whatever the reaction time, the high temperature treatment does not affect the coating. But after  $\text{HNO}_3$  washing all the samples treated without  $\text{Na}_2\text{HPO}_4$  have lost all their organic phase.  $\text{Na}_2\text{HPO}_4$  has a positive effect on the crosslinking: the sorbent obtained in

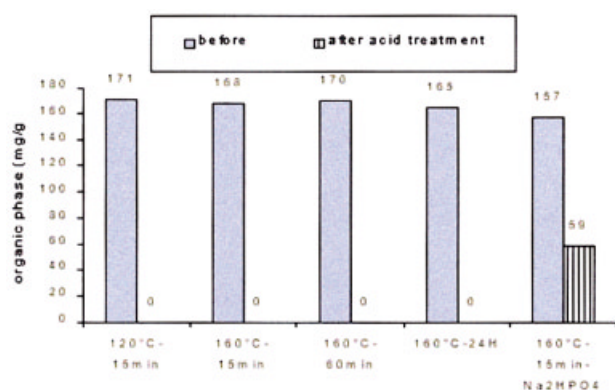


Figure 3 Organic phase coating in relation to different conditions at high temperature. Initial sorbent before temperature treatment was 170 mg/g (1 g SilPEI/2 g EDTA; pH = 6).

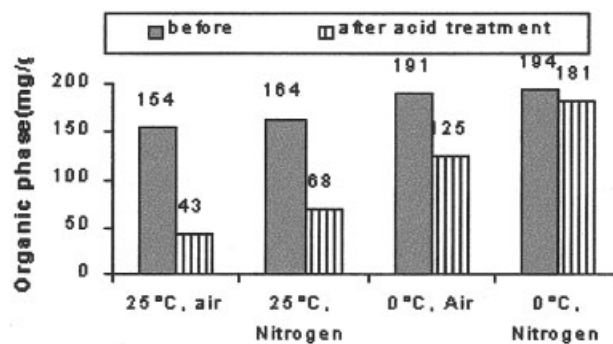


Figure 4 Organic phase coating in relation to different conditions at low temperature (1 g of SilPEI, 1 g of EDTA, 0.5 g of EDAC; time = 10 h, pH = 6).

this way has a better behaviour during acid treatment. Nevertheless, it loses about 110 mg out of 170. This desorbed organic phase corresponds exactly to the amount of PEI coated. As expected  $\text{Na}_2\text{HPO}_4$  promotes reactions between EDTA carboxyl groups but not between EDTA and PEI. The sorbents obtained in this way will contain only one type of chelating groups and will have probably a smaller chelating activity spectrum.

*Test at low temperature and in inert atmosphere:* Usually, in peptide synthesis amide formation is undertaken in organic solvents at a low temperature. In fact, carbodiimides are sensitive to temperature and oxidation. Operating at ambient temperature decreases the energy cost as well as the carbodiimide coupling efficiency.

To decrease the quantity of EDAC, various tests were undertaken, the results of which are shown in Figure 4. From these results it was concluded that:

1. Working at low temperature improved the coating step. Indeed, with only half the amount of EDAC (0.5 g) and a shorter contact time (10 h), at 0°C, the immobilized organic phase was the same as that obtained at 25°C under air with 1 g of EDAC and a contact time of 24 h (see Table I).
2. Working at low temperature under nitrogen promoted the crosslinking reaction and thus stability in an acidic medium. The improvement in crosslinking can be attributed to less degradation of the coupling agent; therefore, the same acid stability was obtained using half the quantity of EDAC in half the reaction time.

By using these conditions, gains were made in time and EDAC consumption; however, the conditions of synthesis (0°C, nitrogen) were more expensive or constraining.

*Using citric acid:* Another way to lower the chemical costs of synthesis is to replace EDTA by a triacid such as citric acid (CA), which currently is at least five times

**TABLE II**  
Effect of Reagent on Amount of Organic Phase Immobilized (pH = 6,  $t$  = 24 h,  $T$  = 25°C, air) in the SilPEI/CA system

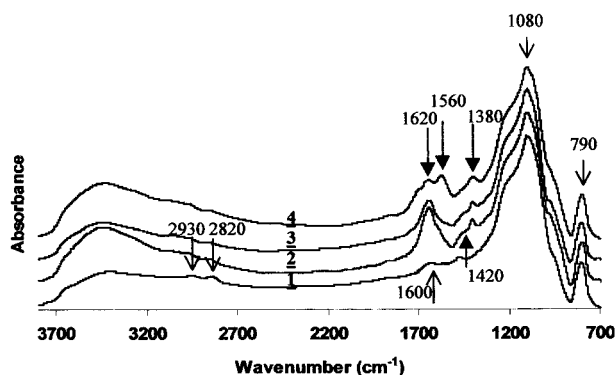
SilPEI (g)	CA (g)	EDAC (g)	Initial	After acid treatment
			Coated (mg/g)	Coated (mg/g)
1	1	1	142	78
1	2	1	156	88
1	3	1	161	93
1	4	1	151	89
1	6	1	141	75
1	1	0.5	153	47
1	1	2	160	103
1	1	3	168	127

less expensive than EDTA. Moreover, CA possesses a hydroxyl group, which offers another possible reaction with the carboxyl group. Table II summarizes the results obtained under different conditions, with EDAC as the coupling agent and CA.

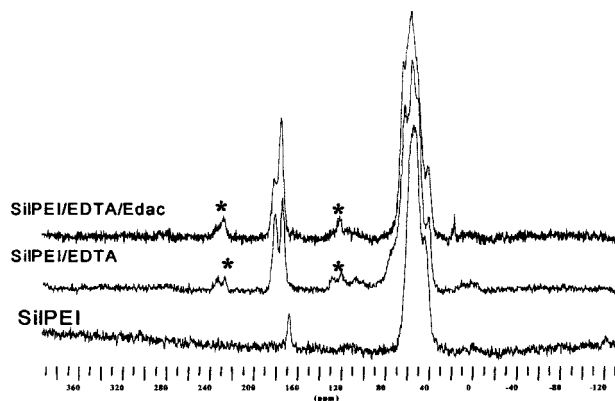
Although there was a greater proportion of CA, expressed in moles (4.76 mmol), than EDTA (2.68 mmol), it is not as good a candidate for coating. For SilPEI/EDTA/EDAC and SilPEI/CA/EDAC, the higher coating amounts were, respectively, 200 and 168 mg/g. Moreover, the acid treatment showed that with CA the organic phase was less anchored around silica. This difference could be attributed to the greater rigidity of CA compared to EDTA. The latter contains methylene groups, which can be flexible spacers between the carboxyl groups. The reaction between amine and carboxyl moieties is then more probable.

#### Characterization of sorbents

Characterization of the EDTA-based sorbents was undertaken. Infrared (IR) and nuclear magnetic resonance (NMR) spectroscopic investigations were performed to identify the different species immobilized



**Figure 5** IR spectra of different sorbents: (1) initial SilPEI, (2) SilPEI/EDTA/EDAC, (3) SilPEI/EDTA/EDAC after acid treatment, (4) SilPEI/CA/EDAC.



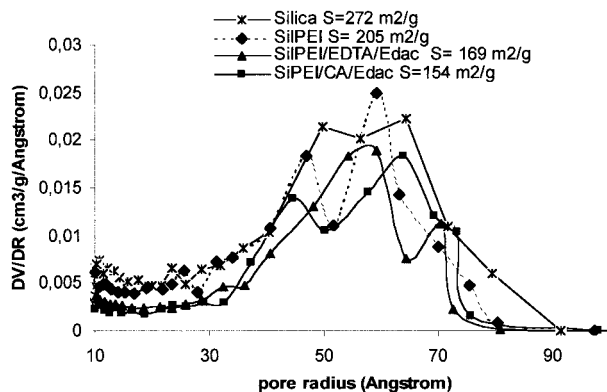
**Figure 6**  $^{13}\text{C}$ -NMR spectra in the solid state for initial SilPEI and sorbents crosslinked by EDTA (\* spinning bands).

onto silica. The IR spectra of initial SilPEI and some crosslinked derivatives are shown in Figure 5.

In all spectra there were bands at 1100 and 790  $\text{cm}^{-1}$  because of, respectively, asymmetric and symmetric stretching of the Si—O—Si vibrations. Coated PEI exhibits weak bands for the  $\text{CH}_2$  groups at 2930, 2820, and 1440  $\text{cm}^{-1}$  and for NH and  $\text{NH}_2$  at 3390 and 1600  $\text{cm}^{-1}$ . These assignments are from a previous work concerning SilPEI.<sup>16</sup>

The presence of a crosslinking agent (EDTA or CA in spectra 2 and 4) produced some characteristic bands:

- The broad band at 3400  $\text{cm}^{-1}$  was more intense because of the C—OH stretching.
- The various new bands between 1680 and 1380  $\text{cm}^{-1}$  could be attributed not only to the C=O from amide bonds (usually in the range of 1700–1630  $\text{cm}^{-1}$ ), the asymmetric and symmetric vibrations of carboxylic acid salt (generally, two bands between 1610 and 1420  $\text{cm}^{-1}$ ), and the C=O from free carboxylic acid (between 1800 and 1650  $\text{cm}^{-1}$ , according to the literature), but also to the N—H



**Figure 7** Pore size distribution and specific area (S) for initial and crosslinked sorbents.

**TABLE III**  
**Elemental Analysis of EDTA-Based Sorbents (Calculated Ratio)**

	Organic phase (mg/g) obtained from TGA	Carbon	Nitrogen	Sodium
PEI		55.8	32.5	0
EDTA <sub>2</sub> Na <sup>+</sup>		35.7	8.3	13.7
SilPEI	110	6.14	3.57	0
SilPEI/EDTA/EDAC	200	11.1	4.3	0.2
	(110 mg PEI + 90 mg EDTA)	(9.3) calc	(4.3) calc	(1.2) calc

or N—CO symmetric stretching between 1630 and 1510 cm<sup>-1</sup>.<sup>17</sup>

There were some differences between EDTA- and CA-based supports. In the EDTA one, the band at 1620 cm<sup>-1</sup>, probably because of C=O from carboxylate, masked the others, whereas in the CA one, a band at 1560 cm<sup>-1</sup>, corresponding to N=CO from amide, emerged.

Spectras 2 and 3 relative to SilPEI/EDTA/EDAC before and after acid treatment are very similar. This confirms the chemical stability of the sorbent crosslinked in the presence of EDAC.

NMR analysis permits confirmation of crosslinking. <sup>13</sup>C-Spectra were recorded in the solid state, but the attributions were compared to liquid-state data.<sup>17</sup> Figure 7 shows the case of sorbents crosslinked by EDTA. The region between 30 and 70 ppm corresponds to the shifts of the different CH<sub>2</sub> and CH groups from PEI as well as from EDTA.

Two bands, at 174 and 181 ppm, appear for EDTA-based sorbents. From the comparison with the NMR spectrum of the EDTA salt form (not given), these bands are attributed to the carbon of, respectively, the carboxylate and carboxylic forms of EDTA. On crosslinking in the presence of EDAC, the band at 174 ppm increased. This could be attributed to the carbon engaged in an amide bond, which usually appears around 170 ppm. Initial SilPEI exhibited a weak band at 168 ppm, which could be assigned to some residual imine groups in PEI.

The TGA analysis only gives the total amount of organic phase coated on silica. Additional information was taken from elemental analysis, giving the respective parts of PEI and EDTA immobilized onto silica (Table III).

The nitrogen ratio (calculated considering 110 mg of PEI and 90 mg of EDTA per gram of sorbent) was consistent with the experimental value. Carbon was a little different, and sodium was very low but could have been exchanged during washing with water.

To conclude this characterization, it was important to check that the chemical treatment had not altered the porosity of the sorbent. In fact, porous silica was originally chosen for its accessibility because of its high porosity and surface area. Specific areas and pore

repartitions were then determined for the main sorbents under study (Fig. 7).

As expected, the specific area significantly decreased during both the coating and crosslinking steps. But it remained high enough to ensure easy exchanges between the coated complexing polymer and the metal ions in solution. Analysis of the pore size distribution showed that the chemical modification of the silica mainly affected the smaller pores (especially the second crosslinking step) and that the pore size distribution was shifted to pores of a larger radii.

## CONCLUSIONS

By varying the conditions of synthesis while keeping in mind the economical and ecological aspects, various sorbents were prepared for use in further metal complexation. They were obtained from an initial PEI-coated silica. This investigation was focused on the stabilization and crosslinking of PEI with multicarboxylic agents. The formation of amide bonds between PEI and carboxylic moieties was necessary to prevent the desorption of the organic layer during the stripping of the metal in an acidic medium. The polyfunctionality of the crosslinking agents was another important parameter to ensure the available chelating groups remained.

The presence of these carboxylate groups immobilized onto a polyamine (as a polymeric spacer) associated with the good porosity of the sorbent is favorable for further metal complexation with a good interaction rate. The removal of heavy metal ions from water by these sorbents will be described in a forthcoming article.

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